

⑪ ① No. 956,783

④⑤ ISSUED Oct. 29, 1974

⑤② CLASS 23-147

C.R. CL.

Re-issue of No. 908,944

Dated Sep. 5, 1972

①⑨ ①①

CANADIAN PATENT

⑥④

PRODUCTION OF CHLORINE DIOXIDE

⑦⑩

Hatherly, David G., Brampton, Ontario, Canada

Granted to Erco Industries Limited, Islington, Ontario,
Canada

②①

APPLICATION No. 201,137

②②

FILED

May 29, 1974

③⑩

PRIORITY DATE

No. OF CLAIMS 15

~~SECRET~~

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

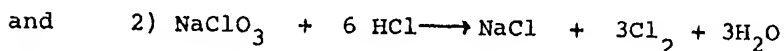
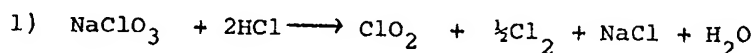
Cette Section est Absente

This invention relates to the production of chlorine dioxide, more particularly to the production of chlorine dioxide from hydrochloric acid-based systems.

Chlorine dioxide is known to be prepared in a variety of ways, involving the reduction of an alkali metal chlorate, generally sodium, utilizing sulphur dioxide, sulphuric acid, chromic sulphate, methanol, sodium chloride and hydrochloric acid as reducing agents. The basic reaction in all such processes is that between chlorate and chloride in the acid solution to produce chlorine dioxide, chlorine and water in accordance with the equation:



The present invention is concerned with the process of making chlorine dioxide where the reducing agent is hydrochloric acid. The basic reactions involved are, in the case where the alkali metal is sodium, :



The two reactions are competing in the reaction solution and reaction (2) becomes significant in cases when there is an excess of hydrochloric acid above the stoichiometry of the reaction (1) in the feed to the reactor. Where such an excess of hydrochloric acid exists, therefore, the quantity of chlorine dioxide produced per mole of sodium chlorate decomposed is reduced. In order to maximize chlorine dioxide production, it is preferred to operate at or near the stoichiometry of equation (1) in the feed to the reactor.

Chlorine dioxide has been produced commercially from hydrochloric acid by the so-called Day-Kesting process disclosed in Canadian Patent No. 461,586 issued December 6, 1947 to Brown



Company. In this process the chlorine dioxide generator consists of a plurality of, generally six, reaction vessels arranged in series. Feed liquor containing sodium chlorate, hydrochloric acid and some sodium chloride is fed to the uppermost of the six reactors, from which the solution cascades by gravity through the remaining reactors. The two bottom reactors are operated at boiling temperature and the steam strips them of chlorine dioxide while the remaining hydrochloric acid is oxidized. Air is introduced into the gas stream from the last two reactors, mixes with the vapour and is bubbled counter-currently through the solution in the reactors three to six.

It has previously been proposed in Canadian Patent No. 782,574 issued April 9, 1968 to Chemech Engineering Limited, to produce chlorine dioxide and chlorine from sodium chloride and hydrochloric acid in a single reaction vessel in place of the cascade six-vessel system used in the Day-Kesting process. In the process described in the above patent, gaseous hydrogen is passed through the reaction vessel to agitate the reaction liquor and as gaseous diluent for the chlorine dioxide and chlorine.

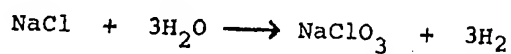
Chlorine dioxide gas in concentrated amounts is spontaneously explosive and in processes of producing chlorine dioxide it is necessary to make some provision for diluting the gases produced in the reaction. Air has commonly been used as in the Day-Kesting operation described above and in the process of Canadian Patent 782,574, hydrogen is the diluent gas.

The process of Canadian Patent 782,574 involves integration of the chlorine dioxide generator with a sodium chlorate cell. The product of the reaction is sodium chloride and the effluent from the chlorine dioxide generator contains sodium chloride as well as unreacted sodium chlorate and hydrochloric acid. This

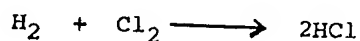
effluent is fed to the chlorate cell wherein at least part of the sodium chloride is converted to sodium chlorate by electrolysis. The solution enriched in sodium chlorate then is returned to the chlorine dioxide generator.

Hydrogen is formed as a by-product of the electrolysis reaction. This gas stream is reacted with chlorine to generate the hydrogen chloride requirement of the chlorine dioxide generator. The hydrogen off-gas from the chlorate cell generally contains minor amounts of chlorine formed by electrolysis of the hydrochloric acid in the cell. This chlorine is combusted in the hydrogen chloride generator.

The main reaction involved in the chlorate cell is:



and the reaction involved in producing hydrogen chloride is:



It will be seen from the above equation (1) that only two moles of hydrogen chloride (as hydrochloric acid in the reaction medium) is required for each mole of sodium chlorate. Therefore, only one-third of the mole quantity of hydrogen produced in the chlorate cell need be combusted with one mole of chlorine to produce the required mole amount of hydrogen chloride, and thereby ultimately the stoichiometric mole amount of hydrochloric acid.

In the process of Canadian Patent 782,574, the excess hydrogen in the hydrogen chloride may be passed through the chlorine dioxide generator as diluent gas for the chlorine dioxide and chlorine. After absorption of chlorine dioxide from the gas mixture, the chlorine and hydrogen are fed to the hydrogen chloride burner.

Operation in this manner leads to a build-up of large amounts of hydrogen in the system. Gas mixtures containing

chlorine dioxide, chlorine and hydrogen may explode, although the risk of explosion is reduced with regard to that where undiluted chlorine dioxide is involved. With larger amounts of hydrogen the extent of damage possible through such an explosion is increased.

10 In order to attempt to control the quantity of hydrogen passing through the chlorine dioxide generator, in the process of Canadian Patent 782,574, a quantity of the gas mixture of hydrogen chloride and hydrogen from the hydrogen chloride combustor is bled from the materials forwarded to the chlorine dioxide generator. The bled mixture is contacted with water to scrub the hydrogen chloride content and the hydrogen gas is vented from the system.

The hydrochloric acid is forwarded to the chlorine dioxide generator. However, forwarding such hydrochloric acid causes further problems since the water content of the hydrochloric acid dilutes the chemicals. Little or no water is evaporated in the chlorine dioxide generator so that the quantity of excess water in the system is built up.

20 As a solution to this problem, in Canadian Patent 782,574, most of the hydrochloric acid formed is not forwarded to the generator. Since less than the stoichiometric hydrogen chloride requirement is now being fed to the generator, it is necessary to produce more hydrogen chloride. While this reduces the quantity of hydrogen to be bled off, it nevertheless increases the chlorine requirement of the system. As a by-product, the hydrochloric acid not forwarded to the generator is collected. In effect, as well as producing chlorine dioxide, the process described in Canadian Patent 782,574 produces hydrochloric acid from chlorine.

30 This may be extremely undesirable in areas where there is limited

availability of chlorine and in areas where there is no economic manner of disposal of the hydrochloric acid.

The process of the present invention provides a system integrating a chlorine dioxide generator and a chlorate cell which does not suffer from the defects of the process of Canadian Patent 782,574 discussed above. In the process of the present invention, the only effluents are chlorine dioxide solution and hydrogen and the only feed streams required are chlorine and water.

10 The present invention employs steam to remove the chlorine dioxide and chlorine from the generator in place of the hydrogen of the process of Canadian Patent 782,574. The use of steam to remove the chlorine dioxide and chlorine in place of hydrogen substantially eliminates the possibility of explosion of the gas mixtures.

 A generator of this type is described and claimed in Canadian Patent Serial Number 913,328. In practice, the alkali metal chlorate generally is sodium chlorate and the generator generally is maintained at the boiling temperature of the solution. Operating at the boiling temperature ensures maximum vaporization from the reaction solution, whereby the product chlorine dioxide and chlorine are rapidly educted from the generator. It is preferred to maintain the temperature in the vessel at a temperature of around 60° to 80°C and a reduced pressure is maintained at these temperatures to bring about boiling.

20

The acidity of the reacting solution is fairly low, generally below about 1N, preferably about 0.5N. An effective range of acidities is about 0.05 to 1N.

30 In accordance with the present invention, the off-gas

hydrogen, possibly containing some chlorine, from the chlorate cell is not all forwarded to the hydrogen chloride burner but only approximately the stoichiometric amount is forwarded. In practice a small excess of hydrogen is preferred so as to ensure complete combustion of the chlorine. The presence of free chlorine in the chlorine dioxide generator reacting solution tends to inhibit the reaction. Excess quantities of about 2% generally are employed. In addition, the excess hydrogen will serve to react with any small quantities of oxygen present in the hydrogen stream or the chlorine stream.

The present invention is further described by way of example with reference to the accompanying drawing which is a flow sheet illustrating one embodiment of the invention.

A chlorine dioxide generator 10 contains a boiling aqueous reaction medium of sodium chlorate and hydrochloric acid. The generator may take several forms and one suitable is described in Canadian Patent 825,084 issued October 14, 1969 to Electric Reduction Company of Canada, Limited, modified as required.

The process of the invention is described with mainly reference to sodium salts, but it is understood the invention is applicable to other alkali metal salts, such as potassium salts.

Sodium chlorate solution is fed to the generator 10 from a chlorate cell 12 through line 14. The hydrogen chloride requirement is fed to the generator 10 from a hydrogen chloride burner 16 through line 18. Water is added to the generator 10 by line 20.

Alternatively, aqueous hydrochloric acid may be fed to the generator 10 by absorbing the hydrogen chloride gas in line 18 in water prior to passage to the generator. It is preferred

to feed gaseous hydrogen chloride to the generator so that the heat of reaction from the burner and the heat of solution of hydrogen chloride in water may be used as part of the heat requirement of the generator. Cooling water for a hydrochloric acid plant is thereby eliminated and the steam load in the generator is reduced.

The generator 10 is maintained under reduced pressure by means not shown. Typical generator conditions are 60°C at 150 to 200 mm Hg.

10 The generator 10 evaporates sufficient water from the reaction medium that product sodium chloride precipitate out in the generator. Any overflow liquor is recycled to the sodium chlorate input line 14. It is preferred, however, to maintain the level of the reacting liquor in the generator 10 at a substantially constant level. This may be achieved by controlling the quantity of water evaporated in the generator.

 Alternatively, the generator 10 may be operated in such a manner that the product sodium chloride is not precipitated. In this embodiment, all of the effluent from the generator is forwarded to the chlorate cell.

20

The sodium chloride is removed from the generator 10 and passed by line 22, preferably after washing to remove entrained reaction liquor, to a sodium chloride dissolver 24. Where washing of the sodium chloride takes place, the spent wash water may be passed to waste or preferably returned to the generator 10.

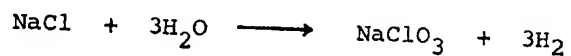
Water fed through line 26 to the dissolver 24 dissolves the sodium chloride to form a sodium chloride solution which is passed by line 28 to the chlorate cell 12. Preferably the minimum quantity of water is employed to dissolve the sodium chloride. The sodium chloride is electrolyzed in the chlorate

30

cell 12 to form sodium chlorate and hydrogen. The sodium chlorate solution is passed by line 14 to the generator 10.

The hydrogen, possibly containing small quantities of chlorine, especially in the embodiment where no sodium chloride is precipitated in the generator and all of the effluents are passed to the chlorate cell 12, passes out of cell 12 by line 30. It is preferred to feed substantially pure sodium chloride solution to the chlorate cell rather than overflow effluent from the generator, since side reactions are minimized with the substantially pure sodium chloride solution, and cell efficiency is thereby increased.

The cell 12 may be of any well known construction and capable of electrolyzing sodium chloride solution to sodium chlorate and hydrogen, in accordance with the equation:



The hydrogen stream 30 is split into two streams, one in line 32 and one in line 34. The stream is split so that approximately one-third of the mole quantity of hydrogen is in line 32 and the remainder in line 34. The hydrogen in line 32 is passed to the hydrogen chloride burner 16 for conversion to hydrogen chloride by burning with chlorine fed through line 36. The hydrogen chloride formed is passed to the generator 10 through line 18.

It is preferred that there be a slight stoichiometric excess of hydrogen in line 32 to ensure complete reaction of the chlorine. The hydrogen chloride in line 18 therefore may contain very minor amounts of unreacted hydrogen.

The hydrogen in line 34 may be vented directly to atmosphere. Where such hydrogen contains chlorine gas, the gas is preferably first fed to a scrubber 38 wherein it is contacted with water fed through line 40 to dissolve out the chlorine. The

hydrogen gas freed of chlorine then may be vented to atmosphere through line 42.

Alternatively, the hydrogen in line 42 or in line 34 may be burned with oxygen, to produce heat to balance energy values, and water which may be used as part of the water requirement of the system. Alternatively, the hydrogen and oxygen may be fed to a fuel cell and electrical energy recovered thereby. In this way, operating economies may be effected.

10 The burner 16 may be replaced by a fuel cell to which the hydrogen in line 32 and the chlorine in line 36 are fed. Hydrogen chloride and electrical power are obtained.

The gaseous products of the generator 10 consisting essentially of chlorine dioxide, chlorine and steam are passed through line 44 to a chlorine dioxide absorber 46. Water is fed to the absorber 46 through line 48 to condense at least part of the water vapour and to dissolve the chlorine dioxide. The liquid effluent of the absorber 46 leaving through line 50 is as aqueous chlorine dioxide solution containing some dissolved chlorine and is suitable for use as feed for a chlorine dioxide bleaching operation, where-
20 in a pulp of cellulosic fibrous material is contacted therewith.

The water fed through line 48 may consist partially of weak chlorine water obtained as effluent from the scrubber 48 in line 52.

The chlorine gas from the absorber 46 containing some water vapour passes through line 54 to the chlorine feed line 36 of the burner 16. Part of the chlorine in line 54 may be passed to the hydrogen line 34 by line 56. This serves to control the quantity of hydrogen being recycled to the generator. Where a stoichiometric excess of hydrogen is fed to the hydrogen chloride
30 burner, albeit minor, the excess will continuously recycle and

build up as in the process of Canadian Patent 782,574 where the problem is much more acute.

Therefore, bleed off of recycle chlorine also bleeds recycle excess hydrogen. The chlorine is not lost to the system since it is recovered in line 52 as an aqueous solution. Using chlorine water in place of pure water to absorb the chlorine dioxide does not appreciably alter the chlorine content of the chlorine dioxide solution in line 50.

It will be seen that the process of the present invention
10 overcomes the practical problems associated with the process of Canadian Patent 782,574. Firstly, since steam is used to remove the chlorine dioxide and chlorine from the generator, the possibility of explosion is substantially minimized. Secondly, since the excess hydrogen is bled off before feed to the hydrogen chloride burner, the build up of excess hydrogen in the system is avoided. Thirdly, gaseous hydrogen chloride may be fed directly to the generator thereby effecting thermal economies. Fourthly, since water is evaporated in the generator, no problems of water imbalance are encountered. Fifthly, no stoichiometric excess of
(20 chlorine is required leading to the formation of by-product hydrochloric acid.

The process employs as raw materials chlorine and water and the products are chlorine dioxide solution, and hydrogen. However, as described above, the hydrogen may be used to produce energy and water, for the process.

Modifications are possible within the scope of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

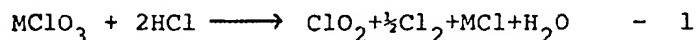
1. A method of forming chlorine dioxide which includes, forming an aqueous reaction medium having an acidity of about 0.05 to 1N and containing an alkali metal chlorate and hydrochloric acid in a reaction zone, heating said aqueous reaction medium to effect reaction between alkali metal chlorate and hydrochloric acid, thereby to generate chlorine dioxide and chlorine, and to evaporate water from said medium, and removing said chlorine dioxide and chlorine from said reaction zone with said evaporated water, said aqueous reaction medium being formed by the steps of: electrolyzing an aqueous solution of an alkali metal chloride to form an aqueous solution of an alkali metal chlorate and hydrogen, feeding said aqueous solution of an alkali metal chlorate to said reaction zone, forming hydrogen chloride by reaction between approximately one-third of the mole amount of said hydrogen and chlorine, and feeding said hydrogen chloride to said reaction zone.
2. The method of claim 1 wherein said reaction medium is heated to its boiling temperature and said reaction zone is maintained under a reduced pressure.
3. The method of claim 2 wherein said alkali metal chlorate is sodium chlorate and sufficient water is evaporated from said reaction medium that product sodium chloride is deposited from said reaction medium.
4. The method of claim 3 wherein said deposited sodium chloride is recovered from said reaction medium and formed into said electrolyzed aqueous sodium chloride solution.

5. The method of claim 1 carried out continuously.

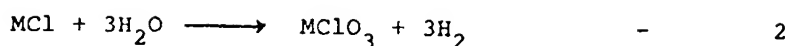
6. The method of claim 1 wherein said chlorine dioxide is separated at least partially from said chlorine and is recovered as an aqueous solution, and the remainder of the chlorine is fed as part of said chlorine reacting with said approximately one-third mole amount of hydrogen.

7. The method of claim 1 carried out continuously and wherein said reaction medium is heated to its boiling temperature, said reaction zone is maintained under a reduced pressure, said alkali metal chlorate is sodium chlorate, sufficient water is evaporated from said reaction medium that product sodium chloride is deposited from said reaction medium, said deposited sodium chloride is recovered from said reaction medium and formed into said electrolyzed aqueous sodium chloride solution, said chlorine dioxide is separated at least partially from said chlorine and is recovered as an aqueous solution and the remainder of the chlorine is fed as part of said chlorine reacting with said approximately one-third mole amount of hydrogen.

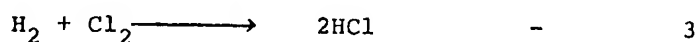
8. A method of forming chlorine dioxide which includes forming an aqueous reaction medium having an acidity of about 0.05 to 1N and containing an alkali metal chlorate and hydrochloric acid in a reaction zone, heating said aqueous reaction medium to effect reaction between said alkali metal chlorate and hydrochloric acid thereby to generate chlorine dioxide and chlorine in accordance with the equation:



where M is an alkali metal, and to evaporate water from said medium, and removing said chlorine dioxide and chlorine from said reaction zone with said evaporated water, said aqueous reaction medium being formed by the steps of: electrolyzing an aqueous solution of an alkali metal chloride to form an aqueous solution of an alkali metal chlorate and hydrogen in accordance with the equation:



where M is an alkali metal, feeding said aqueous solution of an alkali metal chlorate to said reaction zone, splitting said hydrogen into a first stream containing approximately one-third of the mole quantity of said hydrogen and a second stream containing approximately two-thirds of the mole quantity of said hydrogen and forming hydrogen chloride from hydrogen in said first stream by reaction with chlorine in accordance with the equation:

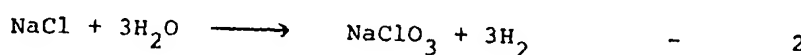


feeding said hydrogen chloride to said reaction zone.

9. The method of claim 8 carried out continuously and wherein said reaction medium is heated to its boiling temperature, said reaction zone is maintained under a reduced pressure, said alkali metal chlorate is sodium chlorate, sufficient water is evaporated from said reaction medium that product sodium chloride is deposited from said reaction medium, said deposited sodium chloride is recovered from said reaction medium and formed into said electrolyzed aqueous sodium chloride solution, said chlorine dioxide is separated at least partially from said chlorine and is recovered as an aqueous solution and the remainder of the chlorine is fed as part of said chlorine reacting with said approximately one-third mole amount of hydrogen.

10. The method of claim 8 wherein said chlorine dioxide is separated at least partially from said chlorine and is recovered as an aqueous solution and gaseous chlorine is recovered, the quantity of hydrogen in said first stream is in slight stoichiometric excess of equation 3, unreacted hydrogen passes into said reaction zone with said hydrogen chloride, is removed with said chlorine dioxide and chlorine and is recovered with said gaseous chlorine.

11. The method of claim 10 wherein said gaseous chlorine containing unreacted hydrogen is fed at least partially to said second stream.
12. The method of claim 10 wherein part of said gaseous chlorine containing unreacted hydrogen is fed to said second stream of hydrogen and part of said gaseous chlorine containing unreacted hydrogen is fed as part of said chlorine reacting with said first stream of hydrogen, whereby the amount of said unreacted hydrogen in said hydrogen chloride may be controlled.
13. The method of claim 11 or 12 wherein said second stream is scrubbed with water to recover said chlorine therefrom as an aqueous chlorine solution.
14. A method of forming chlorine dioxide which comprises continuously forming an aqueous reaction medium having an acidity of about 0.05 to 1N and containing sodium chloride and hydrochloric acid in a reaction zone, continuously maintaining said reaction medium at its boiling temperature while continuously subjecting said reaction zone to reduced pressure to effect reaction between said sodium chlorate and hydrochloric acid thereby continuously to generate chlorine dioxide and chlorine in accordance with the equation:
- $$\text{NaClO}_3 + 2\text{HCl} \longrightarrow \text{ClO}_2 + \frac{1}{2}\text{Cl}_2 + \text{NaCl} + \text{H}_2\text{O} \quad - \quad 1$$
- continuously to evaporate water from said medium, and continuously to deposit sodium chloride from said medium, continuously removing said deposited sodium chloride from said reaction zone, and continuously forming an aqueous solution of said removed sodium chloride; said aqueous reaction medium being continuously formed by the steps of: continuously electrolyzing said aqueous solution of sodium chloride continuously to form an aqueous solution of sodium chlorate and hydrogen in accordance with the equation:



continuously feeding said aqueous solution of an alkali metal chlorate to said reaction zone, continuously splitting said hydrogen into a first stream containing approximately one-third of the mole quantity of said hydrogen and a second stream containing approximately two-thirds of the mole quantity of said hydrogen, continuously forming hydrogen chloride from hydrogen in said first stream by reaction with chlorine in accordance with the equation:



said first stream containing a slight excess of the stoichiometry of equation 3 whereby said hydrogen chloride contains unreacted hydrogen, and continuously feeding said hydrogen chloride containing unreacted hydrogen to said reaction zone; continuously removing said chlorine dioxide and chlorine from said reaction zone with said evaporated water as a gaseous stream containing said unreacted hydrogen, said chlorine dioxide continuously is separated by contact with an aqueous stream at least partially from said chlorine and unreacted hydrogen as an aqueous solution and a gaseous mixture containing chlorine and unreacted hydrogen is continuously recovered, part of said gaseous mixture is continuously fed to said second stream of hydrogen and part of said gaseous mixture is continuously fed as part of said chlorine reacting with said first stream of hydrogen, whereby the amount of unreacted hydrogen in said hydrogen chloride continuously may be controlled, said second stream of hydrogen continuously is scrubbed with water to recover said chlorine therefrom as an aqueous chlorine solution and continuously utilizing said aqueous chlorine solution as at least part of said aqueous stream.

956783

15. The method of claim 14 wherein said second stream of hydrogen after scrubbing is continuously burned to generate water.

